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Project Summary

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Outdoor Smog Chamber Experiments to Test Photochemical Models

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The smog chamber facility of the University of North Carolina (Chapel Hill) was used in a study to provide experimental data for developing and testing kinetic mechanisms of photochemical smog formation. The smog chamber, located outdoors in rural North Carolina, is an A-frame structure covered with Teflon film. Because the chamber is partitioned into two sections, each with a volume of 156 m^3, two experiments can be conducted simultaneously. The dual chamber is operated under natural conditions of solar radiation, temperature, and relative humidity. In this study, 115 dual all-day experiments were conducted using NO_x and various organic species. The organic compounds investigated included various paraffins, olefins, aromatics, and oxygenates, both singly and in mixtures of two or more components.

This report describes the data collected over a three-year period of the study. The experimental procedures and analytical methods used in this study and the limitations and uncertainties of the data are discussed. Guidance for modeling of the data is also given, including a detailed discussion of how to estimate photolytic rate constants from the available ultraviolet and total solar radiation data and how to treat such chamber artifacts as dilution, wall sources and losses of pollutants, and reactivity of the background air.

This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A long-term goal of EPA's research program is to develop urban and regional air quality simulation models (AQSMs) for planning accurate and scientifically-defensible control strategy. Because the pollutants with the greatest health effects are secondary pollutants, formed by chemical reactions occurring in the atmosphere, an understanding of the chemistry that produces these pollutants is critical to the development of AQSMs. In recent years significant effort has been made to explain the chemical transformations that occur in photochemical smog systems and to develop chemical kinetic mechanisms that can be used in the AQSMs to explain the formation of ozone and other secondary pollutants.

Despite the progress that has been made towards an understanding of the chemical processes that lead to the formation of photochemical smog, there is still a need for a comprehensive and well-characterized data base to serve as a benchmark from which kinetic models may be experimentally tested. The purpose of this study was to acquire such a

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data base. Because the ultimate goal of this research is to produce kinetic models that can simulate the processes occurring in the polluted environment, it was important to acquire the data under conditions that were as closely representative as possible of actual atmospheric conditions. For this reason, the dual outdoor smog chamber facility of the University of North Carolina, which is operated using actual sunlight, temperature, and water vapor conditions, was selected for this study. The study was performed by the University of North Carolina (Chapel Hill) under Cooperative Agreement No. 805843.

Procedure

The experiments were conducted in an outdoor A-frame smog chamber covered with Teflon (registered trademark). A Teflon panel divided the chamber into two sections, each with a volume of 156 cm^3. The chamber was purged overnight with the relatively clean air that prevails at the site in rural North Carolina. Shortly before sunrise, the chamber doors were sealed and the reactants of interest were slug-injected into the chamber. The usual procedure was to inject the same concentration of NO_x into both sides of the chamber and then vary the concentration or identity of the hydrocarbon in the two sides of the chamber. The chemical constituents and physical parameters were monitored from the time the reactants were injected until about 6:00 p.m. EDT. A computer-based data-acquisition and control system was used to acquire, process, and record data from the chamber instrument system. Instruments were used to measure NO, NO_2, O_3, PAN, HNO_3, alkyl nitrates, HOOH, CO, individual hydrocarbons, aliphatic and aromatic aldehydes and other oxygenates, such as phenol, acetone, and methylethylketone. Standard meteorological instruments were used to measure solar radiation, ultraviolet radiation, temperature, and dew point.

The experiments took place between May 1977 and August 1980. Of the 115 dual runs conducted in this study, 98 were performed during the June-through-October smog season and 17 were conducted during the winter and spring period from November through May. The reactivities of 18 individual organic compounds and 14 mixtures of two or more organic species were investigated. The organic compounds and the mixtures included in this study are shown in Table 1.

Table 1. Organic Components Used in the Outdoor Smog Chamber Experiments.

Single Components	Mixtures
Formaldehyde	*Formaldehyde/MEK*
Acetaldehyde	*Formaldehyde/Acetone*
Biacetyl	*Formaldehyde/Benzaldehyde*
Methyl glyoxal	
Benzaldehyde	*Ethylene/Formaldehyde*
Methylethylketone	*Ethylene/Acetaldehyde*
Acetone	*Ethylene/Trichloroethylene*
	Ethylene/Trans-2-butene
Ethylene	
Propylene	*Propylene/Formaldehyde*
	Propylene/Acetaldehyde
Butane	*Propylene/Butane*
Pentane	*Propylene/Toluene*
2,3-Dimethylpentane	
Octane	*Toluene/Benzaldehyde*
Toluene	*Alpha-Pinene/Isoprene*
o-Xylene	*Urban Mix*
Isoprene	
Alpha-Pinene	
Butyl nitrate	

Results

The data collected in this study are available in several forms. Included in the project report are hourly data listings and plots of concentration as a function of time for 10 experiments that are representative of the entire data set. In general, these runs have reasonably complete product information, were conducted under favorable sunlight conditions, and offer the modeler a wide range of initial conditions. Also contained in the report are a collection of plots illustrating interesting features of the data set. Included in the report are illustrations of the following:

(1) Selected n-butane, n-pentane, n-octane and 2, 3-dimethylbutane runs and the carbon-containing products identified in these experiments.

(2) Selected aromatic runs, including toluene/NO_x runs, in which the intent of the experiments was to determine the relative yields of benzaldehyde and cresol and to identify ring-cleavage products such as methyl glyoxal.

(3) Experiments demonstrating the effect of adding formaldehyde or acetaldehyde to the propylene/NO_x system.

(4) Experiments to assess the effect of relative humidity on the propylene/NO_x system. In these experiments the air on one side of the chamber was dried by passing it through refrigeration cooling coils and the other side of the chamber was left undried.

In addition to the data for selected runs that are included in the text of the project report, the data are also available as: (1) a computer-readable magnetic tape containing all data for all 115 dual experiments and (2) a set of microfiche of listings and plots of the entire data base. Both the computer magnetic tape and the microfiche are available through the National Technical Information Service, Springfield, VA, as is the project report (see the ordering information at back).

In addition to a detailed discussion on how to access and use the data, the report also contains a complete description of the chamber facility, the procedures and analytical methods used in the study, and the uncertainties and limitations of the data base. Guidance

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for modeling of the data is also given including detailed discussions of how to treat light intensity data, rates of loss of O_3 and NO_x to the chamber walls, walls as a source of free radicals, chamber dilution, temperature and water vapor data, and reactivity of the background air.

Conclusions

Smog chamber data collected in this study were supplied to two model development groups for analysis under EPA Contract Nos. 68-02-3281 and 68-02-3479. The analysis of these data by the two modeling groups resulted in the development of improved kinetic models of photochemical smog formation. The purpose of the project report is to make the experimental data available to the scientific community at large to enable other researchers and modelers to further the development of chemical transformation models.

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The complete report, entitled "Outdoor Smog Chamber Experiments to Test Photochemical Models," (Order No. PB 82-198 508; Cost: $22.50, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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